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Comment on “CO_2 Utilization Feasibility Study Dimethyl Carbonate Direct Synthesis Process with Dehydration Reactive Distillation”

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Sir: The paper[1] presents a detailed analysis of the process design for direct synthesis of dimethyl carbonate. In the paper, the reaction considered, which produces dimethyl carbonate, was:

$$CO_2 + 2CH_3OH \rightarrow C_3H_6O_3 + H_2O \tag{1}$$

To model the reactor conditions in the process design, an equilibrium-based model was fit to experimental data found in the literature. The purpose of the present correspondence is to highlight two potential issues with the equilibrium expression used to model the relationship between temperature and the equilibrium constant for the direct synthesis reaction.

In the paper,[1] data from Bian et al.[2] was used to develop an equilibrium expression to model the relationship between temperature and the equilibrium constant for the direct synthesis of dimethyl carbonate (DMC) in the vapor phase at 15 bar. Bian et al.[2] studied the direct synthesis reaction over a Cu-Ni graphite nanocomposite catalyst at varying temperatures and pressures. However, two potential issues were identified with the equilibrium expression: (1) the data used to fit model parameters are taken at 12 bar, but the model was applied to model reactor conditions at 15 bar, and (2) the reported model parameters do not fit the experimental data.

To demonstrate the first point, it is assumed herein that Figure 3a,[2] which reports the dependence of methanol conversion and DMC selectivity over a temperature range of 353 K to 403 K at 12 bar, is used to develop the model. MATLAB image analysis functions, "imread" and "impixel", are used to extract methanol conversion data from Figure 3a.[2] Because the basis for the model in Wu and Chien is not reported, a mole fraction and partial pressure basis are considered using the data.[1] Specifically, the equilibrium constant for the reaction (1) is calculated using a mole fraction and partial pressure basis using the following equations:

$$K_{eq,mol\ frac} = \frac{y_{\mathrm{C_3H_6O_3}} y_{\mathrm{H_2O}}}{y^2_{\mathrm{CH_3OH}} y_{\mathrm{CO_2}}} = \frac{n_{\mathrm{C_3H_6O_3}} n_{\mathrm{H_2O}} n}{n^2_{\mathrm{CH_3OH}} n_{\mathrm{CO_2}}} = \frac{X^2(3-X)}{4(1-X)^3} \tag{2}$$

$$K_{eq,part\ pres} = \frac{P_{\mathrm{C_3H_6O_3}} P_{\mathrm{H_2O}}}{P^2_{\mathrm{CH_3OH}} P_{\mathrm{CO_2}}} = \frac{y_{\mathrm{C_3H_6O_3}} y_{\mathrm{H_2O}}}{y^2_{\mathrm{CH_3OH}} y_{\mathrm{CO_2}} P} = \frac{n_{\mathrm{C_3H_6O_3}} n_{\mathrm{H_2O}} n}{n^2_{\mathrm{CH_3OH}} n_{\mathrm{CO_2}} P} = \frac{X^2(3-X)}{4(1-X)^3 P} \tag{3}$$

where $K_{eq,mol\ frac}$ is the equilibrium constant using a mole fraction basis, $K_{eq,part\ pres}$ is the equilibrium constant using a partial pressure basis, y_i is the vapor mole fraction of the ith component, P is the total pressure, P_i is the partial pressure of the ith component, X is the conversion of methanol, n is the total number of moles, and n_i is the number of moles of the ith component.

Figure 1 shows the $\ln(K_{eq})$ data from Figure S1[3] compared to the computed $\ln(K_{eq})$ using methanol conversion data extracted from Figure 3a[2] for a mole fraction (Eq. 2) and partial pressure basis (Eq. 3). The data extracted from Figure S1[3] closely matches the calculated equilibrium constant using a mole fraction basis, suggesting that: (1) Figure 3a[2] was in fact the source of data used to fit the equilibrium expression and (2) the basis used in calculating the equilibrium constant was mole fraction. In Figure 1, small differences

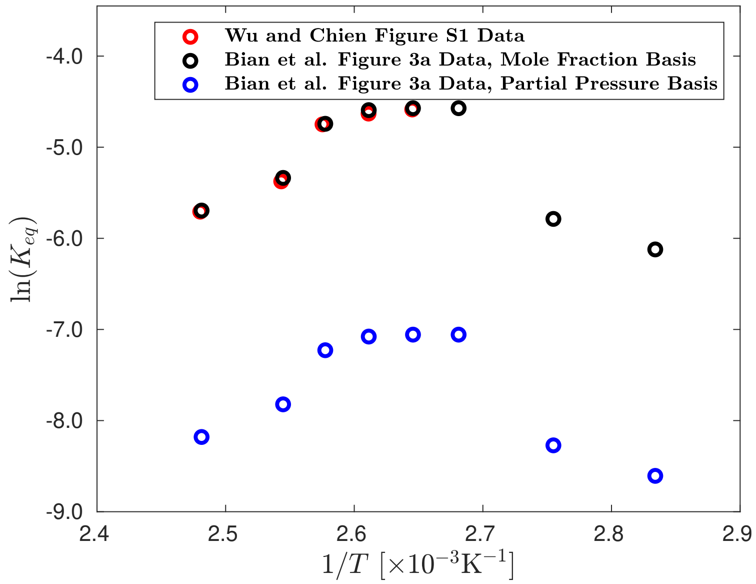

Figure 1: Equilibrium constant versus the inverse temperature extracted from Figure S1 of Wu and Chien[3] along with the equilibrium constant with the temperature computed using Eqs. 2-3 and conversion data extracted from Bian et al.[2] All data was extracted using MATLAB image analysis.

between the computed values of $\ln(K_{eq})$ from the data of Bian et al.[2] and that reported in Wu and Chien[3] are likely attributable to imprecisions in MATLAB image analysis due to low resolution of figures and differences in pixel selection.

Regarding the model validity, the data presented in Figure 1 was based on the methanol conversion for experiments at 12 bar[2] . However, Bian et al. also explores the effect of varying pressure between 8 bar and 15 bar at an unspecified constant temperature in Figure 3b.[2] Between 12 and 15 bar, the conversion of methanol remains relatively constant, while DMC selectivity remains constant above 13 bar. While the results in Bian et al.[2] suggest that the reaction compositions may not change for pressures between 12 and 15 bar, it is unclear if this result is applicable to the entire temperature range studied in Figure 3a. Therefore, a mole fraction basis equilibrium model fitted based on the data shown in Figure 3a[2] and applied to model the equilibrium constant at 15 bar and over a temperature range may result in inaccuracies for some temperatures. Further model validation may be needed to ensure that the resulting equilibrium expression is appropriate at 15 bar and over the temperature range considered.

Nonetheless, if an assumption is made that the conversion data of Figure 3a of Bian et al.[2] is valid at 15 bar over the temperature range of 378 K to 403 K and that the data is from equilibrium conditions, an equilibrium expression may be fit using the data to model the behavior of the direct synthesis reaction over a Cu-Ni graphite nanocomposite catalyst. In particular, the following expression was considered[1] where the model parameters A, B, and C were fit:

$$\ln(K_{eq}) = A + B/T + CT \tag{4}$$

The parameters reported in Wu and Chien[1] are $A = -201.9$, $B = 43088$ K, and $C = 0.22$ K^{-1}. Figure S1 of Wu and Chien[3] shows the experimental data plotted versus the inverse of the temperature along with the reported model. Again, MATLAB image analysis functions "imread" and "impixel" are used to extract the data points in Figure S1[3] and are shown in Figure 2. Additionally, the curve is plotted in Figure 2 with Eq. 4 and the parameters reported.[2]

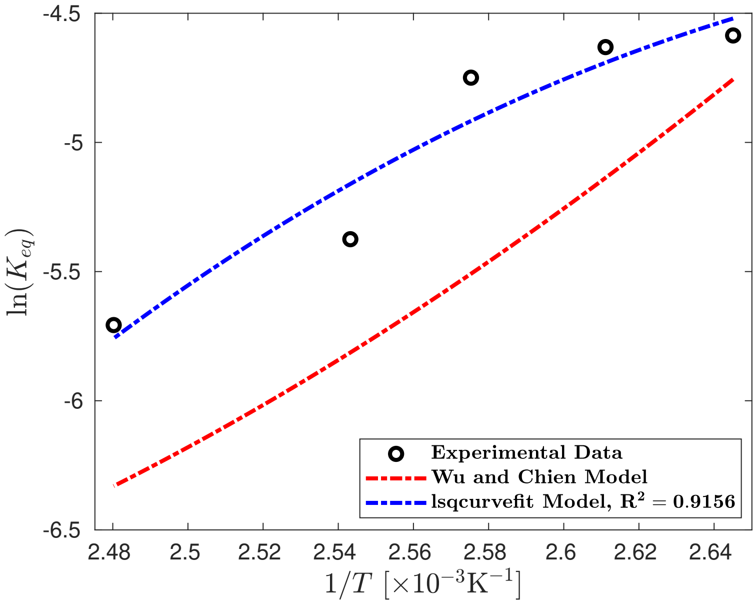

Figure 2: Equilibrium constant versus the inverse temperature extracted from Figure S1 of Wu and Chien[3] plotted with Eq. 4 using parameters reported in Wu and Chien[1] and parameters from MATLAB the "lsqcurvefit". The data was extracted using MATLAB image analysis.

A brief visual comparison between the data of Figure S1 and Figure 2 demonstrates that the error associated with approximating the data from an image analysis of Figure S1 is minimal. Figure 2 shows the experimental data along with the model of Eq. 4 with model coefficients reported in Wu and Chien. There is a noticeable discrepancy between the model with parameters reported in Wu and Chien (shown in Figure 2) and the curve plotted in Figure S1. While the model curve shown in Figure S1 seems to fit the data well, the reproduced model curve shown in Figure 2 is clearly different than that reported in Figure S1.

A separate multivariate linear regression was performed using the "lsqcurvefit" function in MATLAB which yielded parameters of $A = 223$, $B = -40700$ K and $C = -0.32$ K^{-1} and an R^2 value of 0.9156. In contrast to the model with reported parameters,[1] the model with the resulting parameters from MATLAB fits the experimental data well, which is shown in Figure 2. While the magnitudes of the reported parameters[1] are comparable to the magnitudes of the parameters reported here, the signs of all parameters differed. A separate plot was generated to test whether a negative sign is missing in the left hand side of Eq. 4, which was presented in Wu and Chien,[1] however the resulting curve poorly fit the data. Therefore, the parameters reported here appear to be more appropriate based on the experimental data considered.

Nomenclature

A Parameter of the equilibrium constant model (unitless)

B Parameter of the equilibrium constant model (K)

C Parameter of the equilibrium constant model (K^{-1})

K_{eq} Reaction equilibrium constant (unitless)

n_i Moles of species i (mol)

P Pressure (bar)

T Temperature (K)

X Conversion of methanol (unitless)

y_i Vapor mole fraction of species i (unitless)

Supporting Information Available

Supplementary material to this correspondence including the code to reproduce the figures at `https://github.com/danyjiang/ech158c`.

References

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